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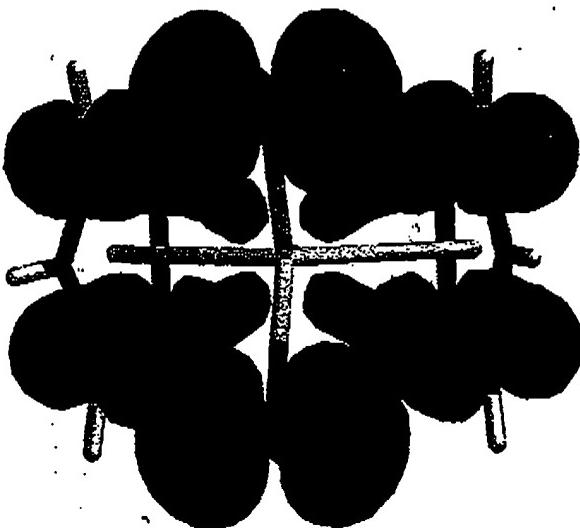
POLYMER SCIENCE

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second edition



JOEL R. FRIED

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1.3 Molecular Weight

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Following IUPAC recommendations, copolymers are named by incorporating an italicized connective term between the names of monomers contained within parentheses or brackets or between two or more polymer names. The connective term designates the type of copolymer (as indicated for six important classes of copolymers in Table 1-5).

Table 1-5 Scheme for Naming Copolymers

Type	Connective	Example
Unspecified	-co-	Poly[styrene-co-(methyl methacrylate)]
Statistical*	-stat-	Poly(styrene-stat-butadiene)
Random	-ran-	Poly[ethylene-ran-(vinyl acetate)]
Alternating	-alt-	Poly[styrene-alt-(maleic anhydride)]
Block	-block-	Polystyrene-block-polybutadiene
Graft	-graft-	Polybutadiene-graft-polystyrene

*A statistical polymer is one in which the sequential distribution of the monomeric units obeys statistical laws. In the case of a random copolymer, the probability of finding a given monomeric unit at any site in the chain is independent of the neighboring units in that position.

1.3 MOLECULAR WEIGHT

1.3.1 Molecular-Weight Distribution

A typical synthetic polymer sample contains chains with a wide distribution of chain lengths. This distribution is seldom symmetric and contains some molecules of very high molecular weight. A representative distribution is illustrated in Figure 1-8. The exact breadth of the molecular-weight distribution depends upon the specific conditions of polymerization, as will be described in Chapter 2. For example, the polymerization of some olefins results in a molecular-weight distribution that is extremely broad, while it is possible to polymerize some polymers, such as polystyrene, with nearly monodisperse distributions under laboratory conditions. Therefore, it is necessary to define an average molecular weight to characterize an individual polymer sample as detailed in the following section.

1.3.2 Molecular-Weight Averages

For a discrete distribution of molecular weights, an average molecular weight, \bar{M} , may be defined as

$$\overline{M} = \frac{\sum_i N_i M_i^\alpha}{\sum_i N_i M_i^{\alpha-1}} \quad (1.1)$$

where N_i indicates the number of moles of molecules with a molecular weight of M_i and the parameter α is a weighting factor that defines a particular average of the molecular-weight distribution. The weight, W_i , of molecules with molecular weight M_i is then

$$W_i = N_i M_i. \quad (1.2)$$

Molecular weights that are important in determining polymer properties are the number-average, \overline{M}_n ($\alpha = 1$), the weight-average, \overline{M}_w ($\alpha = 2$), and the z-average, \overline{M}_z ($\alpha = 3$), molecular weights.

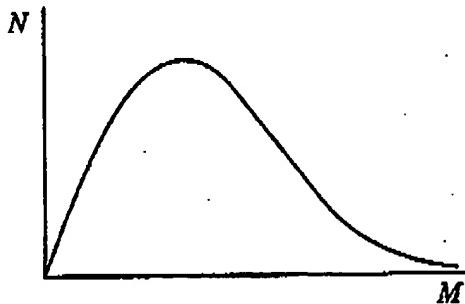


Figure 1-8 A typical distribution of molecular weights shown as a plot of the number of moles of chains, N_i , having molecular weight M_i , against M_i .

Since the molecular-weight distribution of commercial polymers is normally a continuous function, molecular-weight averages can be determined by integration if the proper mathematical form of the molecular-weight distribution (i.e., N as a function of M) is known or can be estimated. Such mathematical forms include theoretical distribution functions derived on the basis of a statistical consideration of an idealized polymerization, such as the Flory, Schultz, Tung, and Pearson distributions,⁴ (see Problem 1.3) and standard probability functions, such as the Poisson and logarithmic-normal distributions.

It follows from eq. 1.1 that the number-average molecular weight for a discrete distribution of molecular weights is given as

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1.3 Molecular Weight

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$$\bar{M}_n = \frac{\sum_{i=1}^N N_i M_i}{\sum_{i=1}^N N_i} = \frac{\sum_{i=1}^N W_i}{\sum_{i=1}^N (W_i/M_i)} \quad (1.3a)$$

where N is the total number of molecular-weight species in the distribution. The expression for the number-average molecular weight of a continuous distribution function is

$$\bar{M}_n = \frac{\int_0^\infty NM dM}{\int_0^\infty N dM} \quad (1.3b)$$

The respective relationships for the weight-average molecular weight of a discrete and a continuous distribution are given by

$$\bar{M}_w = \frac{\sum_{i=1}^N N_i M_i^2}{\sum_{i=1}^N N_i M_i} = \frac{\sum_{i=1}^N W_i M_i}{\sum_{i=1}^N W_i} \quad (1.4a)$$

and

$$\bar{M}_w = \frac{\int_0^\infty NM^2 dM}{\int_0^\infty NM dM} \quad (1.4b)$$

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In the case of high-molecular-weight polymers, the number-average molecular weight is directly determined by membrane osmometry, while the weight-average molecular weight is determined by light scattering and other scattering techniques as described in Chapter 3.

A measure of the breadth of the molecular-weight distribution is given by the ratios of molecular-weight averages. For this purpose, the most commonly used ratio is \bar{M}_w/\bar{M}_n , which is called the *polydispersity index* or PDI.⁴ The PDIs of commercial polymers vary widely. For example, commercial grades of polystyrene with a \bar{M}_n of over 100,000 have polydispersities indices between 2 and 5, while polyethylene synthesized in the presence of a stereospecific catalyst may have a PDI as high as 30.* In contrast, the PDI of some vinyl polymers prepared by "living" polymerization (see Chapter 2) can be as low as 1.06. Such polymers with nearly monodisperse molecular-weight distributions are useful as molecular-

* New metallocene-catalyzed polymerizations can produce polyolefins and other polymers with very controlled structures and narrow-molecular-weight distributions (see Section 2.2.3).

Free-volume contribution:

$$\bar{v}_1 = \frac{1.145}{15.17(1.28)0.04081} = 1.445$$

$$\bar{v}_M = \frac{1.1447(0.1) + 1.0906(0.9)}{15.17(1.28)[0.04081(0.1) + 0.04808(0.9)]} = 1.1920$$

$$\ln \alpha_1^{FV} = 3(1.1) \ln \left[\frac{1.445^{1/3} - 1}{1.1920^{1/3} - 1} \right] - 1.1 \left[\left(\frac{1.445}{1.1920} - 1 \right) \left(1 - \frac{1}{1.445^{1/3}} \right)^{-1} \right] = 0.528$$

Total activity of benzene:

$$\ln \alpha_1 = -1.483 + 0.302 + 0.528 = -0.653; \alpha_1 = 0.520$$

These results show that the residual or enthalpic contribution to the activity is relatively small compared to the combinatorial contribution. This should be expected on the basis of the non-polar nature of PIB and benzene. As shown by a comparison of experimental activities with calculated values in Figure 3-11, UNIFAC-FV very accurately predicts the activity of benzene in PI due to the extensive parameterization of UNIFAC for many compounds.

3.3 MEASUREMENT OF MOLECULAR WEIGHT

As discussed in Section 1.3, commercial synthetic polymers have broad distributions of molecular weight, and it is therefore necessary to report an average molecular weight when characterizing a sample. There are three important molecular-weight averages—number-average (\bar{M}_n), weight-average (\bar{M}_w), and z-average (\bar{M}_z). Absolute values of \bar{M}_n , \bar{M}_w , and \bar{M}_z can be obtained by the primary characterization methods of osmometry, scattering, and sedimentation, respectively. In addition to these accurate but time-consuming techniques, there are a number of secondary methods by which average molecular weights can be determined provided that polymer samples with narrow molecular-weight distributions are available for reference and calibration. The most important of these secondary methods is gel-permeation chromatography (GPC), sometimes called size-exclusion chromatography (SEC). This method is capable of determining the entire molecular-weight distribution of a polymer sample from which all molecular-weight averages can be determined. Another widely used secondary method is the determination of intrinsic viscosity from which the viscosity-average molecular weight can be determined. The viscosity-average molecular weight (\bar{M}_v) normally

lies between \bar{M}_n and \bar{M}_w . The principles behind both primary and secondary methods for molecular-weight determination are discussed next.

3.3.1 Osmometry

Membrane Osmometry. The osmotic pressure, Π , of a polymer solution may be obtained from the chemical potential, $\Delta\mu_1$, or equivalently from the activity, a_1 , of the solvent through the basic relationship

$$\Delta\mu_1 = RT \ln a_1 = -\Pi V_1 \quad (3.96)$$

where V_1 is the molar volume of the solvent. Substitution of the Flory-Huggins expression for solvent activity (eq. 3.34) into eq. 3.96 and subsequent rearrangement gives

$$\Pi = -\frac{RT}{V_1} [\ln(1-\phi_2) + \phi_2 + \chi_{12}\phi_2^2]. \quad (3.97)$$

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Simplification of this relation can be achieved by expansion of the logarithmic term in a Taylor series (see Appendix E) and the substitution of polymer concentration, c , for volume fraction, ϕ_2 , through the relationship

$$\phi_2 = cv \quad (3.98)$$

where v is the specific volume of the polymer. Substitution and rearrangement give the expression

$$\frac{\Pi}{c} = \frac{RT}{M} \left[1 + \left(\frac{Mv^2}{V_1} \right) \left(\frac{1}{2} - \chi_{12} \right) c + \frac{1}{3} \left(\frac{Mv^2}{V_1} \right) c^2 + \dots \right] \quad (3.99)$$

The classical van't Hoff equation for the osmotic pressure of an ideal, dilute solution

$$\frac{\Pi}{c} = \frac{RT}{M}, \quad (3.100)$$

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may be seen as a special or limiting case of eq. 3.99 obtained when $\chi_{12} = 1/2$ and second- and higher-order terms in c can be neglected (i.e., for dilute solution). For high-molecular-weight, polydisperse polymers, the appropriate molecular weight to use in eq. 3.99 is the number-average molecular weight, \bar{M}_n . Equation 3.99 can then be rearranged to give the widely used relation

In addition to determination of molecular weight, measurement of intrinsic viscosity can also be used to estimate chain dimensions in solution. The mean-square end-to-end distance is related to intrinsic viscosity through the relationship³⁷

$$\langle r^2 \rangle = \left(\frac{M[\eta]}{\Phi} \right)^{2/3} \quad (3.122)$$

where Φ is considered to be a universal constant ($\Phi \approx 2.1 \pm 0.2 \times 10^{21} \text{ dL mol}^{-1} \text{ cm}^{-3}$) known as the *Flory constant*.

3.3.4 Gel-Permeation Chromatography

One of the most widely used methods for the routine determination of molecular weight and molecular-weight distribution is gel-permeation chromatography (GPC), which employs the principle of size-exclusion chromatography (sometimes referred to as SEC) to separate samples of polydisperse polymers into fractions of narrower molecular-weight distribution. Basic instrumentation for GPC analysis is shown in Figure 3-21. Several small-diameter columns, typically 30 to 50 cm in length, are packed with small, highly porous beads. These are usually fabricated from polystyrene (crosslinked with a small fraction of divinylbenzene as a comonomer) or the packing may be porous glass beads that are usually modified with an ether or diol linkage. Pore diameters of the beads may range from 10 to 10^7 \AA , which approximate the dimensions of polymer molecules in solution. During GPC operation, pure prefiltered solvent is continuously pumped through the columns at a constant flow rate, usually 1 to 2 mL min^{-1} . Then, a small amount (1 to 5 mL) of a dilute polymer solution ($<0.2 \text{ g dL}^{-1}$) is injected by syringe into the solvent stream and carried through the columns. Polymer molecules can then diffuse from this mobile phase into the stationary phase composed of solvent molecules occupying the pore volumes. The smallest polymer molecules are able to penetrate deeply into the interior of the bead pores, but the largest molecules may be completely excluded by the smaller pores or only partially penetrate the larger ones. As pure solvent elutes the columns after injection, the largest polymer molecules pass through and finally out of the packed columns. These are followed by the next largest molecules, then the next largest, and so on, until all the polymer molecules have been eluted out of the column in descending order of molecular weight. Total sample elution in high-resolution columns may require several hours.

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3.3 Measurement of Molecular Weight

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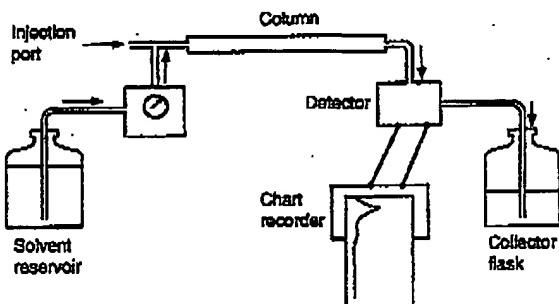


Figure 3-21 Gel-permeation chromatography (GPC). (Harry Allcock and Frederick W. Lampe, *Contemporary Polymer Chemistry*, 2nd ed., ©1990, p. 396. Reprinted by permission of Prentice Hall, Englewood Cliffs, NJ.)

weight and employs the separate sampling. Basic columns, which are usually made of glass, are used with an injection port, pure rate, usually (<0.2 ml/min). Polymers composed of small units are able to pass through the column and are then collected.

The concentration of polymer molecules in each eluting fraction can be monitored by means of a polymer-sensitive detector, such as an infrared or ultraviolet device. Usually, the detector is a differential refractometer, which can detect small differences in refractive index between pure solvent and polymer solution. A signal from the detector is recorded (either by a chart recorder or digitally) as a function of time, which for a fixed flow rate is directly proportional to the elution volume, V_r . A representative GPC chromatogram for a commercial polystyrene sample is shown in Figure 3-22.

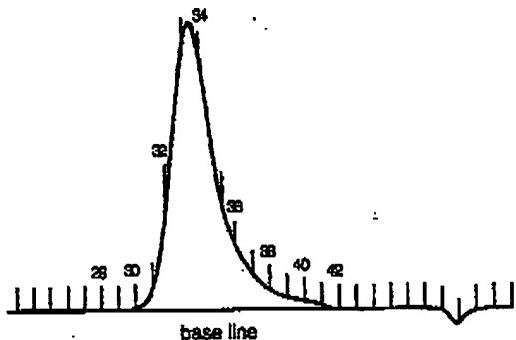


Figure 3-22 GPC chromatogram of polystyrene in tetrahydrofuran at 2.0 mL min^{-1} . Vertical marks represent elution counts. The negative peak at high elution counts may be due to a low-molecular-weight impurities, such as stabilizer, water, or dissolved air. (Adapted from *Introduction to Physical Polymer Science*, L. H. Sperling, Copyright ©1986 John Wiley & Sons. This material is used by permission of John Wiley & Sons, Inc.)

For a given polymer, solvent, temperature, pumping rate, and column packing and size, V_r is related to molecular weight. The form of this relation can be found only by comparing elution volumes with those of known molecular weight and narrow molecular-weight distribution, under identical conditions. Usually, only polymer standards of polystyrene and a few other polymers such as poly(methyl methacrylate) that can be prepared by anionic "living" polymerization (see Section 2.2.2) are available commercially for this purpose. Such standards are available with molecular weights ranging from about 500 to over 2 million with polydispersities as low as 1.06. Since different polymer molecules in the same solvent can have different dimensions, care must be exercised when using polystyrene standards to calibrate elution volumes of other polymers for which standards are not available. The most exact although demanding procedure is to use a universal calibration curve, as illustrated in Figure 3-23.

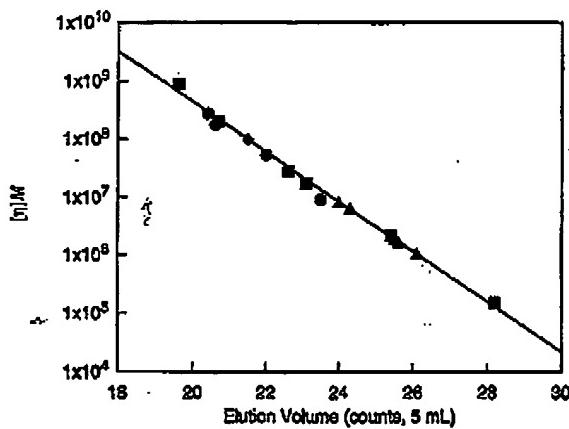


Figure 3-23 Universal GPC calibration curve showing data points for polystyrene (■), poly(vinyl chloride) (△), polybutadiene (◆), and poly(methyl methacrylate) (●) standards in tetrahydrofuran. Line gives best fit of polystyrene data.²³

The universal calibration approach is based on the fact that the product $[\eta]M$ is proportional to the hydrodynamic volume of a polymer molecule in solution (see eq 3.122). This hydrodynamic volume is the effective molecular volume as seen by the pore sites. Universal calibration can be used if the Mark-Houwink constants (see eq. 3.117) are known for both the standard and unknown polymer samples in the same solvent and at the same temperature.

In the calculation of molecular-weight averages, the signal strength (i.e., peak height in Figure 3-21) is proportional to W_i (eq 1.2). Once a proper calibration curve is available to relate V_r to the molecular weight (M) of the calibration standard, direct calculation of all molecular weights— \bar{M}_n , \bar{M}_w , \bar{M}_z , and even \bar{M}_{z+1} —and, therefore, polydispersities

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($\overline{M}_w/\overline{M}_n$ or $\overline{M}_z/\overline{M}_n$) is possible, typically by commercially available software. Recently, on-line coupling of GPC with low-angle light-scattering instrumentation (Section 3.3.2) has enabled rapid on-line computation of molecular weight without the need for separation calibration of the elution curve.

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ABOUT THE AUTHOR

JOEL R. FRIED is Professor of Chemical Engineering and Past Director of the Polymer Research Center, and Head of the Department of Chemical and Materials Engineering at the University of Cincinnati. He has authored over 125 journal articles and several patents and book chapters and serves as Editor of *Polymer Contents* and a member of the

Editorial Boards of *Polymer* and the *Journal of Polymer Engineering*.

His research interests include computational polymer science and membrane science and technology. He holds a B.S. degree in biology.

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